

REPUBLIC OF AUSTRIA  
PATENT NO. 391 131 B

Int. Cl. <sup>5</sup> :	C 04 B 16/02 C 04 B 16/06
File No.:	2937/86
Filing Date:	November 4, 1986
Beginning of Patent Term:	February 15, 1990
Publication Date:	August 27, 1990
Documents Cited:	DE-A-3423286 DE-A-2829759 DE-A-2158654 DE-A-2026700 DE-C-846524 CH-A-636831 GB-A-2105636

MIXTURE FOR PRODUCTION OF MOLDED ARTICLES, ITS USE AND MOLDED  
ARTICLES FORMED FROM IT

Patent Holder:	Eternit-Werke Ludwig Hatschek AG A-4840 Vöcklabruck, Upper Austria (Austria)
----------------	--

A mixture is proposed for the production of fiber-containing, preferably hydraulically bound molded articles, especially according to the wet method, that contain in the conventional manner at least one binder, cellulose fibers and optionally other fibers, especially organic synthetic fibers and/or fibrils, as well as optionally reactive and/or inert inorganic fillers, as well as optionally tempering water, in which cellulose fibers directly treated with at least one known hydrophobizing sizing agent for cellulose fibers and/or cellulose fibers in addition to at least one sizing agent for cellulose fibers that binds cellulose fibers are present, as well as the use of this mixture in a method, especially a wet method, to form molded articles in which the pressed or unpressed molded articles are subjected before, during or after setting to curing at temperatures up to about 220°C, especially between 60 and 180°C, during a period of up to about 45 h,

especially 8 to 40 h, and finally the molded articles are formed from the mixtures, preferably according to the stated method.

The invention concerns a mixture for the production of fiber-containing, preferably hydraulically bound molded articles, especially according to the wet method, which contain in the conventional manner at least one binder, cellulose fibers and optionally other fibers, especially organic synthetic fibers and/or fibrils, as well as optionally reactive and/or inert inorganic fillers, as well as optionally tempering water, as well as its use and molded articles formed from it.

Such material mixtures, also called charges, can contain the conventional additives and auxiliaries, like plasticizers, setting controllers, especially setting accelerators, flocculents, elastifying agents and/or the like, in addition to binders, fibers and/or fibrils and optionally fillers. All these known and subsequently explained components are not to be considered as absolutely encompassed by the above definition of the mixture.

These mixtures, if they cure hydraulically, are tempered at least with the necessary amount of water and, during the wet method, after preliminary drainage, are subjected to shaping, in which a compression process optionally occurs and the molded articles are allowed to cure, in which case process heat is preferably supplied from the outside and/or hardening heat is stored and the molded articles can also be cured in a moist atmosphere and under increased pressure.

For example, preshaped boards are arranged on impact plates, the loaded impact plates are assembled into a stack, the stack is tightened together and then heat cured in an autoclave. Additional possibilities are the simultaneous action of compression and heat, in which the action of heat can begin already before the action of pressure in particularly favorable fashion, for example by using preheated impact plates; loaded molding plates and molding plate stacks without pressing can also be used and curing carried out, for example, in a tunnel furnace without excess pressure.

The use of different fiber types and reactive and nonreactive fillers is known and has been investigated in a variety of ways. For example, AU-PS 515 151 describes an asbestos-free mixture for the production of fiber cement products that consists of cement,  $\text{SiO}_2$  and cellulose fibers, in which 6-12, especially 8 wt% cellulose fibers are present, at least some of which are fibrillated so that the fiber additive overall has a freeness (beating degree) of 350 to 600 Csf. The mixture is processed wet and cured, for example, in an autoclave.

EP-A 0 068 742 (corresponding to GB-A 2 105 636) concerns a method for the production of asbestos-free molded articles, for example, a cladding or roofing plate, in which an aqueous suspension is formed during drainage, which contains, with respect to dry substance,

50-90% cement, 5-40% highly reactive pozzolanic silica and 5-15% cellulose fibers and in which a reaction between the cement and the silica is allowed to occur by air curing. Untreated cellulose fibers are used and 18-35° SR is stated as freeness.

A highly reactive pozzolanic silica, one with at least 80%  $\text{SiO}_2$  content and preferably with a BET surface area of at least 15,000, especially at least 25,000  $\text{m}^2/\text{kg}$ , is proposed. Use of such silicas as an additive to conventional concrete, as well as the pozzolanic reaction between the  $\text{Ca}(\text{OH})_2$  liberated during hydration of the cement and the silica is already well known. The molded articles according to EP-A 0 068 742 can contain additional reinforcing fibers, as well as powdered, granular or flake-like or laminar fillers. Inorganic fibers, for example, glass or mineral wool fibers, and organic fibers, for example, polypropylene fibers, are mentioned as reinforcing fibers.

The molded articles according to EP-A 0 068 742 can, if necessary, be pressed to increase their density and are then heat cured. For this purpose, the molded articles are fed either through an at least 60°C heating tunnel and a relative atmospheric humidity of at least 85% with a residence time of preferably at least 24 h or cured in air merely by the liberated heat of reaction. In the latter case, sealing and heat insulation of the plate stack is recommended in order to prevent heat and moisture losses.

A similar method is described in EP-A 0 127 960. Fiber-reinforced molded articles with a density of at least 600  $\text{kg}/\text{m}^3$ , for example, flat or corrugated boards, are produced therein which an aqueous suspension that contains (with respect to dry substance) 5 to 30% fibers, at least 5% of which are cellulose fibers, 15 to 50% ultrafine silica dust with a specific surface area of 5 to 200  $\text{m}^2/\text{g}$ , and 20 to 80% lime and/or a lime-containing material, as well as 0 to 40% additive, is prepared and during drainage green compacts are formed from it, which are then autoclaved, optionally after pressing and precuring. Materials that liberate lime in the presence of water, like portland cement, are mentioned as "lime-containing material." Synthetic inorganic fibers, like mineral wool, glass, carbon and steel fibers, synthetic organic fibers, like polyester, polyvinyl, polyvinyl alcohol, polyethylene, polyacrylonitrile and polyacrylamide fibers and natural organic fibers, like cellulose fibers, are mentioned in addition to the cellulose fibers that absolutely must be present.

Fillers, like mica, vermiculite, kieselguhr, perlite, expanded clay, diatomite and ground quartz, silica-containing sand and fly ash, colorants, agents for waterproofing, setting and curing accelerators, like calcium chloride and aluminum sulfate, flocculents and dispersants, filter substances, like wollastonite crystals, organic and inorganic plasticizers and fiber dispersants, like hydrophilic inorganic colloidal particles, like hydrophilic silica with a specific surface area greater than 100  $\text{m}^2/\text{g}$ , as well as treated or untreated colloidal particles, are mentioned among the optionally present additives.

Autoclave treatment occurs according to EP-A 0 127 960 at temperatures between 100 and 240°C, preferably 130 to 190°C; the green molded articles, in which supports, blocks, tubes and flat or corrugated boards are mentioned as molded articles, can be pressed, i.e., subjected to mechanical pressure treatment, and precured, especially at 20 to 100°C and a relative atmospheric humidity of 60 to 100% for 6 to 24 h.

All these proposals go in the direction of replacing asbestos fibers with replacement fibers in which the fiber additives, on the one hand, are to be considered in their effect in the finished molded article, and, on the other hand, in their effect as process fibers, i.e., their effect during production of the molded articles, especially in the wet method.

It has turned out in experiments along these lines that of the replacement fibers, cellulose fibers are the most comparable to asbestos fibers; plastic fibers yield a higher impact toughness in the finished product than cellulose fibers, which, however, exhibit better properties as process fibers.

On the other hand, it is known that all merely physically bound water in fresh concrete is up to 100% recovered as pore volume in cured concrete and it is both practically and theoretically impossible to produce pore-free concrete, since even chemically bound water after hydration is completed leaves behind about 25% of its original volume as pore volume.

In high-cellulose fiber-containing fiber concrete molded articles, a poor suitability for external use and high porosity was found; cellulose fibers might also still have the property in the cement matrix of absorbing moisture and releasing it, and loosening and bursting of the matrix were observed, which suggest this property, since strong swelling of the fibers is always connected with moisture absorption, especially in an alkaline medium.

The task was therefore to modify cellulose fibers so that, on the one hand, they entrain as little physically bound water in the fresh concrete as possible with retained binder retention, so that no pore spaces form around the fiber and, on the other hand, the fibers exhibit no tendency to swell in the matrix composite.

To solve this task, it is proposed according to the invention to use cellulose fibers directly treated with at least one known hydrophobizing sizing agent for cellulose fibers in the production of fiber cement molded articles, optionally together with other fiber additives and/or fiber-like additives, like fibrils, in which cellulose fibers so treated and/or cellulose fibers in addition to a sizing agent that bonds to cellulose fibers are present in the mixture.

DE-PS 3 423 286 does not concern a mixture for the production of hydraulically bound molded articles, but a soft material surface sealing that contains as filler a mixture of pyrogenic silica with feldspar, precipitated silica and/or dolomite and has the form of a fibrous web that can contain 5 to 15 wt% sulfate pulp and is prebound based on latex (i.e., organically)

(nitrile-butadiene latex) and then impregnated with liquid polybutadiene and the impregnation finally crosslinked by peroxide.

DE-OS 28 29 759 concerns a mass based on mineral fibers ( $\text{SiO}_2$ ) and silicate fibers with a content of clay (for example, kaolin) that is organically bound to so-called cardboard plates. It can contain 0.5 to 7 wt%, preferably 1 to 5 wt% cellulose fibers, with respect to dry substance. The cellulose fibers in these known plates have a completely different purpose than in fiber-cement plates; the products cannot be compared.

DE-OS 21 58 654 concerns a method for the production of cement-bound wood chips or similar boards in which water and cement is admixed with the chips, a blank is formed and this is pressed. This method (see for example the first paragraph on page 2 of the document) is not a wet method in the sense of the fiber cement technique. The proposal for increasing the strength of the fiberboards produced according to the German unexamined patent application involves addition of a mixed polymer dispersion (especially PVC mixed polymer) to the mixture of wood chips, cement and water. This mixed polymer is not a cellulose fiber sizing agent, but forms a resin coating on the chips that does have a certain water-repellant effect, but serves essentially as a binder, on the one hand, for the chips, so that the cement particles also adhere better, and, on the other hand, for the entire board, which permits a reduction in the amount of cement.

In similar fashion, DE-OS 20 26 700, like DE-OS 21 58 654, concerns a laminated and compressed board that consists of ground and chopped reed grass to which wood chips or sawdust are added after spraying of a sizing mixture in the corresponding desired density and are pressed. This is a dry method in which a nonhomogenous laminated product is produced and has nothing to do with a wet method for the formation of a hydraulically bound fiber cement product.

DE-PS 846 524 concerns a method for the production of fiber cement products, for example, an conventional Hatschek wet method in which pretreated cellulose is used. For this purpose the cellulose fibers are first coated essentially with resins that react with the hydroxyl groups of the cellulose. The aminoplastic resin stated for this purpose, like melamine, urea and polyethylimine resins (probably polyethyleneimine resins correctly) react as cationic resins with the cellulose – for example, melamine resin is a typical creaseproof finishing for cotton fabric – but are not known in the paper industry as sizing agents, but as retention, wet strengthening and dry strengthening agents and have no hydrophobizing effect. This was also obviously recognized according to DE-PS 846 524, since it is stated there that after coating of the fiber with the mentioned resins, they can additionally be treated with water-repellent substances, in which rosin, the classic paper sizing agent, is mentioned as an example.

DE-PS 846 524 therefore only discloses the use of cellulose fibers in a wet method for the production of fiber cement products that are first provided with a resin coating and then treated with a hydrophobizing paper sizing agent. The paper sizing agent therefore serves for

hydrophobizing of the articles with a plastic surface (optionally cured beforehand and with little load-bearing capacity) which has a cellulose fiber as core.

On the other hand, it is proposed according to the invention to treat cellulose fibers directly with a known hydrophobizing sizing agent for cellulose fibers; which represents a one-stage procedure with full retention of the load-bearing capacity of cellulose fibers and is neither disclosed nor suggested by the prior art.

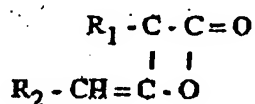
CH-PS 636 831 concerns the addition of an aqueous, anionic bitumen emulsion to fiber cement mixtures that are processed according to the wet method and which can contain cellulose fibers in addition to mineral fibers, like asbestos fibers. The procedure is such that the anionic bitumen emulsion is added to the formed fiber/cement suspension in water, which must have increased stability so that it does not break immediately because of the strongly alkaline medium. After breaking of the emulsion, the fine bitumen particles are distributed uniformly in the product so that a sealing effect occurs so that dependency of the cellulose fibers to absorb moisture is counteracted. It is obvious that a bitumen emulsion is not a hydrophobizing sizing agent that bonds to cellulose fibers, as is prescribed according to the invention.

In selecting the sizing agent, which is supposed to bond to the cellulose fibers only during tempering of the mixture, a reactive sizing agent is primarily considered, which is attracted to the cellulose fibers in an alkaline medium.

Reactive sizing agents are also generally preferred that can be referred to as internal sizing agents and react with specific cellulose groups and therefore are not absorbed in arbitrary amounts on the fibers, at least not without using additional means.

Internal sizing agents based on diketenes are proven to be particularly effective, since they are very alkaline-resistant and produce the same sizing.

Such internal sizing agents are known for cellulose fibers; the alkyldiketenes Aquapel 360, Basoplast 200 D and Teroson GR 940 are mentioned as examples of commercial diketenes. The diketenes, actually ketene dimers, correspond to the general formula



in which  $R_1$  and  $R_2$  independently of each other represent an organic hydrophobic hydrocarbon group with 8 to 40 carbon atoms.

The organic hydrophobic hydrocarbon groups  $R_1$  and  $R_2$ , which are suitable for sizing of cellulose material, are those in which the hydrophobic group is a higher alkyl group with at least

about 8 carbon atoms, like decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, tetracosyl and pentacosyl groups, and also higher alkyl groups that contain up to about 40 carbon atoms, if this is desired, although those with about 12 to 30 carbon atoms are preferred. The corresponding alkenyl groups with about 8 to 40 carbon atoms are also suitable. Examples include decenyl, tridecenyl, heptadecenyl, octadecenyl, eicosenyl and tricosenyl groups. Aralkyl-, alkaryl- and alkyl-substituted cycloalkyl groups with at least 8 carbon atoms can also be used, for example, 4-tert-butylphenyl, octylphenyl, nonylphenyl, dodecylphenyl, tridecylphenyl, pentadecylphenyl, octadecylphenyl, heneicosylphenyl, nonylcyclopropyl, dodecylcyclobutyl, tridecylcyclopentyl, tetradecylcyclohexyl, pentadecylcycloheptyl and octadecylcyclohexyl groups. Each of these alkyl, alkenyl, alkaryl and alkylcycloalkyl groups can contain noninterfering inert substituents. Among these inert substituents, ether, carboalkoxy, alkyloxy, aryloxy, arylalkyloxy, keto(carbonyl)-tert-amide groups, etc. can be mentioned. As examples of groups that preferably should not be present to a greater extent in the hydrophobic group, hydroxyl groups, amide groups that contain amide hydrogen, primary and secondary amino groups, unstable halogens and carboxyl groups and other acid groups can be mentioned. It is obvious to those skilled in the art which groups can be used, if undesired secondary reactions are to be avoided.

Preferably  $R_1$  and  $R_2$  independently of each other represent an alkyl group with 12 to 30 carbon atoms. The ketene dimers can also be a mixture of at least two of the aforementioned compounds.

The ketene dimers are produced conventionally, for example, by conversion of thionyl chloride and carboxylic acids that contain the aforementioned hydrophobic hydrocarbon groups in order to produce the corresponding acid chloride, which are then dimerized to ketene dimers by splitting off of hydrogen chloride.

The ketene dimer group reacts with the hydroxy group of the cellulose molecules so that an irreversible bond results between the cellulose molecule and the organic hydrophobic hydrocarbon groups in the ketene dimer molecules. When ketene dimers are added to an aqueous suspension of cellulose fibers as so-called beater additives, the ketene dimers are dispersed in water by means of dispersants.

It is also known that the yield during the reaction between ketene dimers and cellulose fibers rises if the aqueous dispersions of ketene dimers contain a cationic dispersant. When these cationic dispersions are used, the ketene dimer particles acquire improved affinity relative to the slightly negatively charged cellulose fibers so that the reaction yield is improved.

Any conventional water-soluble or water-dispersible cationic polymers can be used as cationic dispersants. These have thus far been described as retention agents, wet strength agents or dry strength agents in paper production, and polyethyleneimine, polyacrylamide,

polyvinylpyrrolidone, polyamide-polyamine resin or its epichlorohydrin-modified derivative can be mentioned as examples for the preferred cationic, water-soluble or water-dispersible polymers. Particularly favorable results were achieved with cationic polyvinylpyrrolidone, whereas cationic starch that is used in paper production very often as a cationic dispersant can adversely affect setting of the cement matrix in the present context.

The combination of ketene dimer and cationic dispersant can be modified to improve the yield during the sizing reaction in that alkylhydroxyalkylcellulose is additionally added, which also acts as dispersant. The alkylhydroxyalkylcellulose incorporated in the dispersal system preferably includes a water-soluble or water-dispersible cellulose with a Brookfield viscosity in the range of 20 to 12,000 cP in a 2% solution at a temperature of 20°C. As examples of appropriate types of cellulose, those in which the alkyl group is a lower alkyl group, preferably methyl or ethyl and in which the alkylhydroxy group is a hydroxy-lower alkyl group, like ethylhydroxy or propylhydroxy group can be mentioned. The hydrocarbon chain in the hydroxyalkyl group can also be interrupted by one or more oxygen atoms. It can also be expedient to use a mixture of these cellulose ethers.

Cellulose fibers treated with ketene dimers can also be used very favorably as a fiber additive for fiber cement products, if a water-soluble dicyandiamide/formaldehyde condensate is also used for the treatment which, for example, is obtained by conversion of dicyandiamide, formaldehyde and an ammonium salt so that the aqueous treatment phase of the cellulose fibers contains the ketene dimer, the condensate and one of the aforementioned cationic emulsifiers.

Instead of or in addition to the aforementioned formaldehyde condensate, a cationic resin can also be used which is the reaction product of epichlorohydrin with a condensate from cyanamide or dicyandiamide and the polyalkylene polyamine.

Likewise, instead of or in addition to ketene dimers, other hydrophobizing, cellulose-reactive sizing agents can be used, for example, hydrophobic organic isocyanates. The choice and adjustment of the components of the aqueous treatment phase is guided according to the resistance of the obtained "sizing" in the strongly alkaline reacting cement matrix, in addition to the hydrophobizing effect.

Among the organic isocyanates, mostly those having at least 12 and preferably 14 to 36 carbon atoms are considered. Examples include rosin isocyanate, dodecyl isocyanate, octadecyl isocyanate, tetradecyl isocyanate, hexadecyl isocyanate, eicosyl isocyanate, docosyl isocyanate, 6-ethyldecyl isocyanate, 6-phenyldecyl isocyanate and polyisocyanates like 1,18-octadecyl diisocyanate and 1,12-dodecyl diisocyanate in which a long-chain alkyl group is linked with two isocyanate groups.



The amount of pretreated cellulose fibers used in the mixtures according to the invention is not critical, but it was found that excellent properties of the composite matrix are obtained even with limited additives and low porosity is also observed with large amounts of additives.

Particularly favorable results are achieved with charges that have already increased strength as a pure cement matrix, like those containing condensed silica.

Particularly advantageous mixtures characterized by the fact that 1-4.5% fibers and/or fibrid, 50-80% binder, 10-30% inert fillers and 5-20% reactive fillers, especially condensed silica are present in the dry mixtures.

It was also surprisingly found that the mixtures according to the invention, especially when they have a low fiber content, can be processed wet very favorably and produce an excellent matrix composite of the molded article formed with it if they contain at least one nonfibrous plastic, especially in the form of a dispersion, preferably with a solids content of 40 to 50%, preferably a dispersion in an acrylic base. The content then lies especially in the range of 1 to 8% plastic with respect to the dry mixture. For example, all plastic dispersions that can be added to cement in order to improve its processability and wet strength, as well as reduce the vulnerability to cracking and/or increase elasticity, are then suitable. For example, a plasticizer-free aqueous copolymer dispersion from an acrylic acid ester and styrene with a solids content of about 50% is suitable. Pure acrylate dispersions or nonionic self-crosslinking, pure acrylate dispersions with a solids content between 40 and 50% can also be used. Nonionic or anionic dispersion have been shown to be advantageous. In the case of self-crosslinking pure acrylate dispersion, specific catalysts based on oxalic acid or p-toluenesulfonic acid can be used to improve crosslinking. The addition of diethylaminoethanol is also advantageous. Mowilith is mentioned as commercial product for vinyl acetate dispersions and Neo-Cryl for acrylate dispersions.

These plastics are not the ones that are conventionally used for plasticization of water/cement mixtures (for example, "plasticizers" or "super plasticizers").

In addition to pretreated cellulose fibers, synthetic fibers, especially polyvinyl alcohol fibers and/or polyacrylonitrile fibers are optionally used in the mixtures used according to the invention as fiber components. Polyolefin fibers, like polypropylene and polyethylene fibers, as well as polyaramid fibers, can also be used.

Cellulose fibers are then understood to mean all those fibers without consideration of the type of fiber recovery. The following are mentioned as examples:

Cellulose from

- hardwood )

)

wood fibers, especially softwood sulfate pulp (kraft pulp)

- softwood )

- jute            )
- hemp           )
- )       base-stem fibers
- flax            )
- ramie           )
  
- sisal           )
- )       leaf fibers
- abaca           )

wood chips

refiner (mechanical) pulp (MP)

thermomechanical pulp (TMP)

recycling products like scrap paper or paperboard

The term synthetic fibers employed in conjunction with the mixtures according to the invention includes all organic and inorganic fibers, like polyacrylonitrile, polyvinyl alcohol, polyethylene, polypropylene, glass, carbon or ceramic fibers. The length of these fibers advantageously lies between 2 and 8 mm. They are more suitable the thinner their diameter. Fibers with a diameter between 10 and 100  $\mu\text{m}$  are now used. However, the use of thinner fibers is also conceivable.

The addition of fibrils to cement mixtures, especially fiber cement mixtures, is already described, among other places, in AT-PS 355 486; their definition can be taken from this document. Organic fibrils are at issue in particular.

2-4.5% cellulose fibers and 0.5-3.0% polyvinyl alcohol and/or polyacrylonitrile fibers are present in particular in the mixtures according to the invention.

When fibrils are used, mixtures advantageously contain 0.5-1.5% fibrils, 2-3.5% cellulose fibers and 0-1.5% synthetic fibers.

It was also found that very favorable processing and matrix properties are obtained by the use of pretreated cellulose fibers that are additionally loaded with an inorganic filler, in which loading advantageously occurs before sizing.

All reactive or nonreactive fillers in the system are considered as load fillers, which can also be used as additives to the matrix, for example, magnesite, limestone flour, quartz flour, blast furnace slag, trass, brick dust, wollastonite, montmorillonite, bentonite, vermiculite and condensed silica, in which the particle size of the filler lies roughly in the range of conventional

cement finenesses, but finer or coarser products are also possible. Finely divided products are preferred for fiber loading.

Condensed silica (CSF – condensed silica fume) is an industrial dust-like metallurgical waste product that has already been proposed in the cement/fiber cement sector from Si metallurgy; usually with  $\text{SiO}_2$  contents between 75 and 99% and a specific surface area (BET) between 15 and 30  $\text{m}^2/\text{g}$  and it has turned out that it provides very favorable results in the context of the mixtures according to the invention for loading of fiber materials, especially cellulose fibers. In cellulose fibers not only the fibers can be enclosed with a finely divided filler, but also their internal lumen can be loaded according to the so-called lumen loading process. During the use of CSF one proceeds in that the cellulose is first beaten to about 20° SR to 35° SR and part (about double the weighed amount of dry fibers) CSF is added to the fibers suspended in water and agitated under high turbulence. Under these conditions, part of the silica dust particles, among other things, through the bordered pit, penetrates into the lumen of the cellulose fibers under these conditions. By this type of treatment (lumen loading), the fiber is not only enclosed on the outside by CSF, but also filled in the interior. Because of this the lifetime of the cellulose fibers in the product can be lengthened, namely, its acid character means that the immediate surroundings of the cellulose fibers have a lower degree of alkalinity. The degradation of the cellulose fibers observed with entry of air in a strongly alkaline medium is slowed because of this. It could be determined by laboratory experiments that the cellulose fibers had absorbed up to 20% of their own weight of silica particles in their lumen.

Fixing agents for the filler and in the fiber can be used, for example, flocculents, like aluminum sulfate, optionally together with conventional, especially neutral to anionic flocculents. Anionic polyacrylamides (for example, Percol E10 from Allied Colloids or AP45 from Dow Chemical) are preferred as flocculents, which can also be used in general as processing auxiliaries in the wet method.

For sizing, the cellulose fibers are beaten and treated usually at 20-35° SR with the sizing agent. Advantageously, they are dried after treatment and used as a dry fiber component in the production of the mixtures according to the invention. The fibers then need only be beaten further, i.e., finely divided. A particularly advantageous way to use sizing agents in treating cellulose fibers and fiber cement mixtures is one in which the sizing agent is first added during production of the fiber cement charge, in which case sizing occurs, so to speak, in situ during tempering of the charge. It is also possible to carry out treatment with the sizing agent during the production process for the cellulose fibers, especially before their final drying in the course of drainage.

Hydraulic binders are preferably used as binders, i.e., especially those that contain lime or liberate lime. Among the cements, these include portland cement, metallurgical cement and aluminat cement. Gypsums and magnesium oxide binders can also be used.

As already mentioned, mixtures according to the invention can also contain conventional additives and auxiliaries, for example, setting accelerators or retarding agents. The drained products can be pressed but need not be. During curing, heat can be applied to accelerate the chemical reaction between the calcium hydroxide and the CSF. It depends on the corresponding process whether temperatures are chosen below 100°C or above 100°C (autoclave). However, it is important that the relative humidity is more than 95% locally. It is also possible to place boards for curing in water of 40 to 90°C for a specified time, for example 8 to 48 h.

It was also already mentioned at the outset that the mixtures according to the invention can be processed according to all known and common methods in the field of fiber cement technology, and the most significant of these methods were listed. In particular, one proceeds in that the pressed or unpressed molded articles are subjected to curing at temperatures up to about 220°C, especially between 60 and 180°C for a period of up to about 45 h, especially 8 to 40 h before, during and/or after setting.

The molded articles subjected to the action of heat for setting can also simultaneously be subjected to pressing.

The molded articles can also favorably be pressed and then set in a heat column.

Typically, the molded articles can be brought between heated molding plates for setting, in which pressing optionally occurs via these plates.

The heat and optionally pressure treatment can also occur in the conventional manner on molded articles stacked between molding plates.

Typical compositions for mixtures according to the invention are as follows:

Total content of fibers and/or fibrids (for example, cellulose fibers or a mixture of sulfate pulp with one or more synthetic fibers and/or fibrids)	up to 30%, especially 1-12%
Hydraulic binder	50-80%, especially 55-80%
Filler, inert	10-30%
Filler, reactive (CSF)	5-20%
Plastic	up to 8%

The following experiments were run to show the use of pretreated cellulose fibers:

#### Employed materials

- Softwood sulfate pulp, beaten in a PFI melt to 25° SR

- Commercial aqueous alkyldiketene dispersion: Basoplast 200D containing about 6% alkyldiketene
- Tap water: 4-5° German hardness
- Cement water: tap water was mixed with 10 wt% commercial portland cement PZ 275H for 12 h, the solids allowed to settle and the clear water filtered
- Cement: commercial portland cement PZ 275H was used

#### Experiment 1:

30 g cellulose were agitated with a 5% alkyldiketene suspension at 3% stock density for 10 min, made up to 0.5% stock density with cement water and agitated for 1 h. Sheets were then made on a Rapid Kothén sheet former with cement water and dried in vacuum at 53°C.

The sheet so formed had ink penetration times of more than 1 h during testing for the degree of sizing according to Brecht Liebert (an automated ink floating test). Similarly made sheets without alkyldiketene additives broke through within a tenth of a second.

#### Experiment 2:

Production of fiber cement boards:

0.05 g of a commercial aqueous alkyldiketene suspension with about 6% alkyldiketene was added to 10 g of cellulose of 35° SR suspended in about 500 mL water and 120 g cement stirred in after 2 min of agitation. The obtained mass was drained over a screen press, the formed articles stored in an environment at 20°C at 95-100% relative humidity for 28 days.

For a comparative experiment, molded articles were produced according to the method just described, but addition of the diketene suspension was omitted. The water absorption was tested on the hardened samples. It amounts to 24% in the samples without diketene and 11.5% in the samples with diketene.

#### Claims

1. Mixture for the production of fiber-containing hydraulically bound molded articles according to the wet method, which contains a lime-containing or lime-releasing binder, surface-treated cellulose fibers and optionally other fibers, especially organic synthetic fibers and/or fibrils, as well as optionally reactive and/or inert inorganic fillers, as well as optionally tempering water, characterized by the fact that cellulose fibers treated directly with at least one known hydrophobizing sizing agent for cellulose fibers and/or cellulose fibers in addition to at least one hydrophobizing sizing agent for cellulose fibers that bonds to cellulose fibers are present in the mixture.

2. Mixture according to Claim 1, characterized by the fact that cellulose fibers treated with at least one sizing agent that produces a sizing that is resistant in an alkaline medium and/or cellulose fibers in addition to at least one sizing agent for cellulose fibers that is reactive and bonds to cellulose fibers in an alkaline medium are present, in which those based on diketene are used as the sizing agent.

3. Mixture according to Claim 1 or 2, characterized by the fact that up to 30%, preferably 1 to 12%, especially 1 to 4.5% fibers and/or fibrils, 50 to 80% binder, 10 to 30% inert filler and 5 to 20% reactive filler, especially condensed silica, are present in the dry mixture.

4. Mixture according to one of Claims 1 to 3, characterized by the fact that up to 8% of at least one nonfibrous plastic, especially in the form of a dispersion, preferably with a solids content of 40 to 50%, preferably a dispersion based on acrylate, is present in the dry mixture.

5. Mixture according to one of Claims 1 to 4, characterized by the fact that polyvinyl alcohol fibers and/or polyacrylonitrile fibers and/or polyolefin fibers and/or polyaramid fibers are present in addition to cellulose fibers.

6. Mixture according to one of Claims 1 to 5, characterized by the fact that 2 to 4.5% cellulose fibers and 0.5 to 3.0% other fibers, especially polyvinyl alcohol and/or polyacrylonitrile fibers are present.

7. Mixture according to one of Claims 1 to 6, characterized by the fact that 0.5 to 1.5% fibrils, 2 to 3.5% cellulose fibers and 0 to 1.5% synthetic fibers are present.

8. Mixture according to one of Claims 1 to 7, characterized by the fact that cellulose fibers loaded with a filler, especially condensed silica, are present.

9. Mixture according to Claim 8, characterized by the fact that cellulose fibers loaded in an aqueous suspension under high turbulence with a filler, especially condensed silica are present, which are optionally additionally treated with a fixation agent, preferably with aluminum sulfate as flocculent, especially together with a neutral to anionic flocculent, preferably a polyacrylamide.

10. Method, especially wet method, for the formation of molded articles using the mixture according to one of Claims 1 to 9 in which the pressed or unpressed molded articles are subjected to curing at temperatures up to about 220°C, especially between 60 and 180°C, during a period of up to 45 h, especially 8 to 40 h, before, during and/or after setting.

11. Method according to Claim 10, in which molded articles subjected to the action of heat for setting are simultaneously subjected.

12. Method according to Claim 10 or 11, in which the molded articles are pressed and then allowed to set in a heating tunnel.

13. Method according to one of Claims 10 to 12, in which the molded articles are introduced between heated molding plates for setting during which pressing optionally occurs via these plates.

14. Method according to Claim 13, in which heat and optionally pressure treatment occurs on molded articles stacked between molding plates.

15. Molded articles formed from the mixture according to one of Claims 1 to 9.